



Preparation of nanostructured carbon materials

Fernando Pérez-Caballero, Anna-Liisa Peikolainen*, and Mihkel Koel

Institute of Chemistry, Tallinn University of Technology, Akadeemia tee 15, 12618 Tallinn, Estonia

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Abstract. The low-density organic aerogels formed by the supercritical carbon dioxide drying of 5-methylresorcinol–formaldehyde gels are a good source material for the preparation of low-density carbon aerogels with a homogeneous structure. In our research the supercritical drying process was optimized so that the resulting aerogels would not significantly shrink during the process. The density of the resulting 5-methylresorcinol–formaldehyde organic aerogel was as low as 0.1 g/cm^3 , its specific surface area being more than $350 \text{ m}^2/\text{g}$. Also, the pyrolysis of the organic aerogel to get carbon material with a proper structure was optimized in relation to the low rate of the evolution of pyrolysis products during the process. The carbon material obtained had a uniform structure, consisting of sparsely packed particles with a narrow size distribution. The density of carbon aerogels obtained was 0.2 g/cm^3 , their specific surface area being over $700 \text{ m}^2/\text{g}$; the shrinkage was up to 30%. It was also found that the porosity of carbon aerogels could be varied by changing the conditions of synthesis. The aerogels obtained were examined using scanning electron microscopy, infrared spectroscopy, and nitrogen adsorption–desorption analysis.

Key words: materials science, carbon aerogel, supercritical drying, porous material.

INTRODUCTION

To prepare aerogels, which are highly porous materials with very low density and high specific surface area, in the first place a gel, which is composed of the solid and liquid phase independent of each other, is prepared. When the liquid phase is removed from the gel in a non-destructive manner, the solid porous material will be left with approximately the same shape and volume as the original gel. To avoid high capillary pressures within the pores from the surface tension caused by the receding liquid meniscus during the evaporation of liquids, in practice, supercritical extraction (SCE) is used for drying the gels [1].

Pekala et al. synthesized organic hydrogels by the sol–gel polycondensation of resorcinol (1,3-dihydroxybenzene) with formaldehyde (F) and prepared resorcinol–formaldehyde (RF) aerogels by the supercritical drying with carbon dioxide [2]. In Estonia, 5-methylresorcinol (MR) as a by-product of the oil-shale industry is a cheap source material for this purpose. When using MR for the preparation of organic

gels, the similarity to processes where resorcinol and phenol are used was assumed. To obtain gels with the lowest density and minimum shrinkage, the molar ratios of the reagents and experimental conditions have to be varied [3].

Aerogels can be obtained as monoliths, granulates, films, or powders. They can further be pyrolysed in an inert atmosphere at temperatures around 1000°C to obtain carbon aerogels. The RF carbon aerogels have a high porosity ($>80\%$) and large specific surface areas ($400\text{--}900 \text{ m}^2/\text{g}$), which can be increased by the process of activation up to the values of over $2500 \text{ m}^2/\text{g}$ [4]. The new direction in the field of carbon aerogels is the preparation of highly ordered mesoporous carbon materials [5]. Carbon aerogels can be used as adsorbents, materials for chromatographic separation, and electrodes for capacitors or fuel cells [6,7].

The preparation of aerogels starts with the synthesis of aqueous colloidal solutions where the chemical and physical structure of the polymer take shape. Formaldehyde is responsible for the formation of cross-linking aromatic molecules and should be used at a molar ratio of $0.4 < \text{R/F} < 0.7$ since too much formaldehyde remaining induces a collapse of the mesoporous structure and

* Corresponding author, annaliisa@gmail.com

decreases the pore volume of the aerogel prepared [8]. The amount of the catalyst in the solution affects the size of the particles formed as well as and the transparency of gels. Increasing the amount of the catalyst decreases the size of particles and pores and leads to a faster gelation [9].

A basic or acid catalyst can be used for the preparation of gels, but double-catalysed synthesis is considered to be the most effective [10,11]. Under basic conditions, formaldehyde is linked to an aromatic ring to form methylol ($-\text{CH}_2\text{OH}$) groups. The second step with an acid catalyst promotes polycondensation [12]. As for the basic catalysts, it has been shown that the valence and ionic radius of hydrated cations affect the orientation of the reaction path and the rate constant of the polymerization [13]. Besides hydroxides, also carbonates are used as basic catalysts [14].

The addition of formaldehyde takes place in the 2nd, 4th, and 6th positions due to the hydroxyl groups in the 1st and 3rd positions. As 5-methylresorcinol has in addition to two hydroxyl groups a methyl group in the 5th position, a relatively fast gelling in comparison with the resorcinol–formaldehyde gel formation could be expected.

In the case of resorcinol, the usual gelation temperature range used is 50–90°C; the higher the temperature, the faster the gelling [2].

The amount of the solid fraction in the solution is expressed as the molar ratio of water/resorcinol, W/R. Increasing the amount of the solid fraction results in larger pores and a quicker gelling [11].

After the gel is formed and washed with acetic acid the solvent exchange step follows. The water within the pores of the gel is exchanged for the solvent miscible with CO_2 to carry out the SCE effectively.

In the preparation of carbon aerogel the next, last step is the pyrolysis of the organic aerogel. During pyrolysis the organic aerogels maintain the main carbon backbone of the structure. The carbonization affords a carbon aerogel with a highly porous structure, a large specific surface area, and a very low density. During pyrolysis, carbon aerogels also undergo mass loss, which leads to the volumetric shrinkage and densification relative to their pre-carbonized counterparts [15].

MATERIALS AND METHODS

In this study, 96% 5-methylresorcinol (a product of Carboshale, Estonia) was used as a phenolic precursor for organic gel. Formaldehyde (a 37% w/w solution in water) was prepared from paraformaldehyde powder (95%, obtained from Aldrich, Germany). Anhydrous sodium carbonate (99.8%, Riedel-de-Haen, Germany) and acetic acid solution (pH ~ 4) were used as catalysts,

and acetone (99.5%, Riedel-de-Haen, Germany) was used for solvent exchange.

5-Methylresorcinol and formaldehyde aquagels were synthesized using double-catalysed polycondensation. Sodium carbonate (C) was used as the base. The aquagels were obtained by curing the solutions at room temperature for 48 h. The gelation times of the gels prepared were in the range of one to four hours depending on the composition, but the gel was always left for 48 h to enable the curing process to take place. The moulds used were test tubes with an approximate diameter of 1 cm and a length of 10 cm, and the gel occupied 80% of the total volume of the tubes. After that the gel was placed in an acetic acid solution (10 times the volume of the gel piece) and left there for a further 48 h, changing the acetic acid solution every 24 h so that hydrolysis could be favoured as the rate-determining step of the gelation process. The MR–F aquagels prepared had pores filled with water. As it is poorly soluble in CO_2 , the water was replaced by acetone after four days, renewing the latter every 24 h [16]; the amount of the acetone used for each exchange was 10 times the volume of the gel piece.

The drying with CO_2 was performed in three steps. First, the gel was introduced at a pressure of 20 MPa at 25°C for 20 min to fill the pores of the gel with CO_2 and dissolve the acetone within. Then, the exit valve was opened and the extractor was depressurized to 12 MPa, letting the liquid CO_2 flow through the gel at 25°C. The time for the liquid CO_2 flow through the gel was varied from one to two and a half hours. After this step the temperature was raised to 50°C and CO_2 reached the supercritical state. The SCE lasted for two hours. After the extraction was completed, the extractor was slowly depressurized to atmospheric pressure and the MR–F aerogel was obtained.

The supercritical drying was performed using laboratory-made equipment that allows pressures of up to 30 MPa and temperatures of up to 150°C to be achieved.

The pyrolysis of the dried aerogel was performed in a tubular furnace in an inert atmosphere (N_2) at a working temperature of up to 1100°C, and controlled by a Nabertherm Program Controller S19 (Germany). The temperature program of the oven was as follows. The temperature was increased from room temperature at a rate of 10°C/min until it reached 300°C, at which it was kept for 80 min. After that, the temperature was increased again at a rate of 10°C/min until the pyrolysis temperature (700 or 1000°C) was reached. The gels were then left at the pyrolysis temperature for four hours. After pyrolysis, the furnace was left to cool down to room temperature.

The composition and morphology of the organic and carbon aerogels obtained were determined using an EDAX JEOL 6042 analyser, a Leo Supra 35 Scanning

Electron Microscope (SEM), and a Spectrum BX FT-IR System (Perkin Elmer), where IR measurements were obtained in the wavelength range from 4000 to 400 cm^{-1} using the KBr disk method. For nitrogen adsorption analyses, a Sorptometer KELVIN 1042 built by Costech International was used. The volume of the gas (N_2) adsorbed on the surface of the materials at a liquid nitrogen temperature was measured with an accuracy of over 97%. Helium was used as the carrier gas, nitrogen being the adsorptive gas. The Brunauer–Emmet–Teller (BET) theory was used to calculate the specific surface area (S_{BET}), the specific micropore volume (V_{mic}) was calculated according to the t -plot theory, and the pore size distribution, using the Barrett–Johner–Halendar (BJH) theory.

For thermogravimetric analysis SETARAM LabSys 2000 TG/DTA equipment was used. Experiments were performed in a N_2 (99.999%) flow of 100 mL/min at a heating rate of 10 $^\circ\text{C}/\text{min}$ in a Pt crucible. The sample mass was 8.5 mg.

RESULTS AND DISCUSSION

The formation of the gel starts in a colloidal solution where its chemical and physical structure take shape. The concentration of the reactants is given in molar ratios MR/F, MR/C, W/MR. The ratio W/MR describes the amount of the solid fraction in the gel.

In another study, a technical mixture containing 59.6% of 5-methylresorcinol (HoneyolTM, a product of VKG, Estonia) was successfully used for the preparation of aerogels. The preparation process was based on the technology similar to the present one, and is described in detail elsewhere [17].

Supercritical drying of organic gels

The drying process has been proven to be very important for the final appearance and properties of aerogels. However, this process is the least time-consuming step among the other steps in the aerogel preparation: it took place in less than five hours whereas the whole synthesis needed a week to be fully completed. Because of its mild critical parameters (31.1 $^\circ\text{C}$ and 7.4 MPa), availability, and low price [18] CO_2 was used as a fluid.

Before and after the drying, the bulk gels were measured and their radial shrinkage and density were calculated. It was found that the lowest densities and shrinkages characteristic of MR–F aerogels were obtained when using molar ratios MR/F = 0.5, W/MR = 45, and MR/C = 60. At a ratio MR/C = 60 opaque gels with large pores were obtained. This enabled a short drying process and an almost complete removal of the solvent. Removal of the solvent can be assessed by measuring the shrinkage of the gel with the same composition after extended drying time. When the ratio MR/C = 16 was used, the pores of the gels were smaller and acetone was not extracted from the pores so easily. In this case, with a longer period of drying the shrinkage of the gels was less considerable and their density lower. The supercritical extraction four hours longer decreases the shrinkage by 11% and lowers the density more than 1.5 times. The relations between the catalyst amount, the drying time and the density and shrinkage of aerogels can be observed in Table 1.

The effect of the supercritical fluid drying on the porous structure of gels is illustrated in Fig. 1a and 1b.

Table 1. The effect of the catalyst amount and the drying time on the density and shrinkage of aerogels. MR/F = 0.5, W/MR = 45

MR/C	CO ₂ drying regime, h			Supercritical drying		Ambient drying	
	20 MPa, 25 $^\circ\text{C}$	12 MPa, 25 $^\circ\text{C}$	12 MPa, 50 $^\circ\text{C}$	Density, g/cm ³	Radial shrinkage, %	Density, g/cm ³	Radial shrinkage, %
60	0.33	2.5	2	0.21	1	0.46	35
	0.33	2	2	0.21	2	0.46	28
	0.33	1.5	2	0.21	4	0.46	35
	0.33	1	2	0.21	3	0.46	33
16	0.33	2	6	0.58	27	1.35	45
	0.33	2.5	2	0.92	38	1.35	45

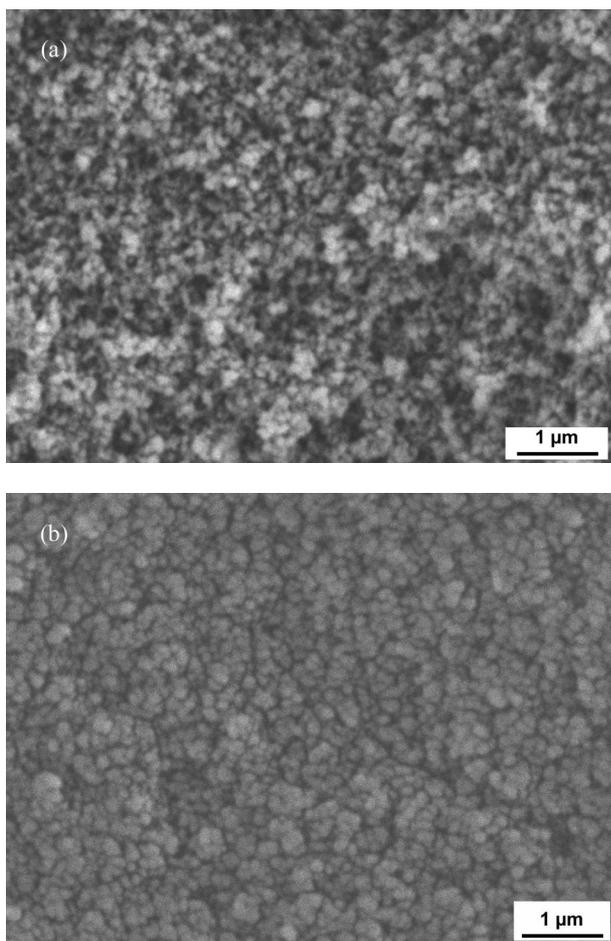


Fig. 1. SEM images of MR-F (MR/C = 60) organic aerogel dried by supercritical CO₂ extraction (a) and under ambient temperature and pressure (b).

With supercritical drying an aerogel with a sparse low-density structure was obtained. Drying at ambient temperature (25 °C) and pressure (1 atm) resulted in dense gel pieces that, due to capillary pressures, even cracked sometimes.

The MR-F gel formed in an acidic medium only was inhomogeneous and attracted no further attention, although its density and radial shrinkage were similar when dried either using SCE or under ambient conditions.

The aerogels were analysed using infrared spectrometry. In basic conditions the transmittance of IR is the lowest at 1000, 1500, and 1400 cm⁻¹. In these regions the IR radiation was absorbed by the substituted 5-methylresorcinol. Acetic acid dissolved part of this monomer turning the colour of the solution yellowish and making the gel more transparent for the IR radiation. The number of methylene (-CH₂- area 2930 cm⁻¹ and 1450 cm⁻¹) and ether bridges (-CH₂-O-CH₂- area 1100 cm⁻¹) was almost equal in the gels prepared in basic and acidic media. The spectrum characterizing the

gels obtained by double-catalysed synthesis shows this type of catalysis not to be more advantageous than the one-step catalysis. However, after pyrolysis the aerogels prepared by double-catalysed base-acid synthesis shrank less and had lower density than those prepared using only the basic catalyst.

BET surface area measurements were carried out using the supercritically dried gels and an ambient dried aerogel. The specific surface area of the SCE dried aerogels is about 30 m²/g larger than that of aerogels dried under ambient conditions.

Pyrolysis of aerogels

Carbon aerogels were prepared by the pyrolysis of organic aerogels in a tubular furnace. During the pyrolysis N₂ flowed through the reactor. The temperature program was adjusted after performing the thermogravimetry of organic aerogel samples (Fig. 2).

The thermogravimetric studies showed that at temperatures of up to 300 °C, the rate of the mass loss of the gels was not as high as above 300 °C. It is for this reason that the heating rate of up to 10 °C per minute was used until reaching this temperature. The gel sample was then kept at 300 °C for one hour before raising the temperature because an exothermic reaction occurs at 300 °C. The temperature was then raised very slowly (2 °C/min) up to 550 °C as several reactions take place below 600 °C. Before raising it further, the temperature was again kept at 550 °C for 30 min and then raised at a rate of 10 °C per minute up to 780 °C. This temperature was taken as the final pyrolysis temperature because no intensive reactions occur above it. The choice of the final temperature depends on the requirements for pore size and specific surface area [19]. Above 780 °C, as the gel mass loss was very small, more time was needed to get a better activation of the gel, though no considerable changes were expected above the final temperature used in this study. There was a mass loss of the gels of over 80% at temperatures below 750 °C and most exo- and endothermic reactions took place at temperatures between 400 and 650 °C.

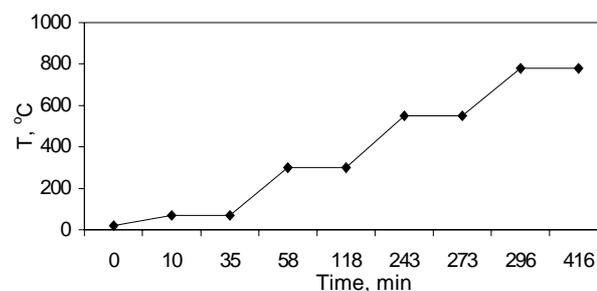


Fig. 2. An optimized pyrolysis program for converting aerogels into carbon aerogels.

The porosity of the gel can be characterized according to pore size. Macroporosity refers to pores greater than 50 nm in diameter and mesoporosity, to pores greater than 2 nm and less than 50 nm in diameter. Microporosity refers to pores smaller than 2 nm.

In this study, the technique used for the evaluation of the pore size distribution (PSD) allowed no study of microporosity. Figure 3, depicting the first derivative of the specific surface area with the pore diameter versus the pore diameter, shows a typical PSD of the carbon aerogel pyrolysed under the optimized temperature conditions and the final temperature of 780 °C as mentioned above. It can be seen that the gel is mainly microporous and mesoporous and only very little macroporosity is observed.

It is interesting to follow how the pore size distribution and BET surface area are affected by the temperature of pyrolysis. A conclusion can be drawn that microporosity decreases with increasing temperature of pyrolysis. Data on the porosity and specific surface area of carbon aerogels are presented in Table 2. It can be seen that in pyrolysed carbon aerogels micropores can be detected and the specific surface area is higher compared to the unpyrolysed aerogel. It must be mentioned that before the pyrolysis organic aerogels were mainly mesoporous, to a smaller extent macroporous, but not microporous whatsoever. It is interesting to note that pyrolysis carried out at an optimized temperature program (final temperature 780 °C) led to carbon aerogels with mainly a microporous structure and the highest specific surface area was obtained.

The size of the pores in the surface of carbon aerogels strongly depends on the composition of the organic gels and conditions of their preparation. The lowest density and specific surface area of the carbon aerogels obtained by our group were 0.2 g/cm³ and 700 m²/g, respectively. Although the facilities available did not allow more thorough analysis of porosity, it can be concluded that the gels prepared were microporous rather than mesoporous, which resulted in a considerably larger surface.

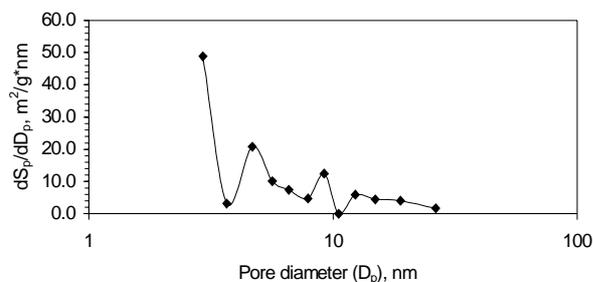


Fig. 3. A typical pore size distribution of the carbon aerogel pyrolysed at 780 °C.

Table 2. Pyrolysis of gel samples under different conditions. MR/F = 0.5, MR/C = 60, and W/MR = 45

Temperature/ pyrolysis program	BET surface area, m ² /g	V _{micropores} , mm ³ /g	Non-micro- porous area, m ² /g	Micro- porosity, %
700 °C	450	130	55	88
1000 °C	290	47	160	45
Optimized at 780 °C	590	165	23	96
Unpyrolysed	140	Not detected	140	0

CONCLUSIONS

5-Methylresorcinol is an appropriate source compound for preparing organic aerogels by base or double-catalysed synthesis. Gels with the minimum shrinkage and density were obtained using molar ratios MR/F = 0.5, MR/C = 60, and W/MR = 45. The whole extraction process took place in less than 3.5 h, the density and shrinkage being 0.2 g/cm³ and 3%, respectively. According to literature data the preparation of RF organic aerogels takes about 8 h or longer and the shrinkage is more considerable. It was also rather easy to manipulate the pore and particle size of the gel. Moreover, gels did not need high temperature for the gelation process. The MR–F gels were solid after an hour.

Optimization of the pyrolysis program allowed the production of carbon aerogels characterized by a larger specific surface area and a higher microporosity. The study of the influence of the pyrolysis temperature and program on the final structure of carbon aerogels revealed the importance of this parameter in the monitoring of the final properties of carbon aerogels.

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REFERENCES

1. Fricke, J. & Tillotson, T. Aerogels: production, characterization, and applications. *Thin Solid Films*, 1997, **297**, 212–223.
2. Pekala, R. W. Low density, resorcinol-formaldehyde aerogels. United States Patent 4873218, 1989.

3. Pérez-Caballero, F., Peikolainen, A.-L., Uibu, M., Kuusik, R., Volobujeva, O. & Koel, M. Preparation of carbon aerogels from 5-methylresorcinol–formaldehyde gels. *Micropor. Mesopor. Mater.*, 2008, **108**, 230–236.
4. Hanzawa, Y. & Kaneko, K. Activated carbon aerogels. *Langmuir*, 1996, **12**, 6167–6169.
5. Liu, C., Li, L., Song, H. & Chen, X. Facile synthesis of ordered mesoporous carbons from F108/resorcinol–formaldehyde composites obtained in basic media. *Chem. Commun.*, 2007, 757–759.
6. Pekala, R. W. Organic aerogels from the polycondensation of resorcinol with formaldehyde. *J. Mater. Sci.*, 1989, **24**, 3221–3227.
7. Tamon, H., Ishizaka, H., Araki, T. & Okazaki, M. Control of mesoporous structure of organic and carbon aerogels. *Carbon*, 1998, **36**, 1257–1262.
8. Tamon, H., Ishizaka, H., Mikami, M. & Okazaki, M. Porous structure of organic and carbon aerogels synthesized by sol-gel polycondensation of resorcinol with formaldehyde. *Carbon*, 1997, **35**, 791–796.
9. Kim, S. Y., Yeo, D. H., Lim, J. W., Yoo, K. P., Lee, K. H. & Kim, H. Synthesis and characterization of resorcinol–formaldehyde organic aerogel. *J. Chem. Eng. Japan*, 2001, **34**, 216–220.
10. Berthon-Fabry, S., Langohr, D., Achard, P., Charrier, D., Djurado, D. & Ehrburger-Dolle, F. Anisotropic high-surface-area carbon aerogels. *J. Non-Cryst. Solids*, 2004, **350**, 136–144.
11. Barral, K. Low-density organic aerogels by double-catalysed synthesis. *J. Non-Cryst. Solids*, 1998, **225**, 46–50.
12. Tamon, H. Carbon aerogels. In *Encyclopedia of Materials: Science and Technology*, 2001, 898–900.
13. Grenier-Loustalot, M. F., Larroque, S., Grande, D., Grenier, P. & Bedel, D. Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics. *Polymer*, 1996, **37**, 1363–1369.
14. Horikawa, T., Hayashi, J. & Muroyama, K. Controllability of pore characteristics of resorcinol–formaldehyde carbon aerogel. *Carbon*, 2004, **42**, 1625–1633.
15. Baumann, T. F. & Satcher, J. H. Jr. Template-directed synthesis of periodic macroporous organic and carbon aerogels. *J. Non-Cryst. Solids*, 2004, **350**, 120–125.
16. Li, W. C., Lu, A. H. & Guo, S. C. Control of mesoporous structure of aerogels derived from cresol–formaldehyde. *J. Colloid Interface Sci.*, 2002, **254**, 153–157.
17. Peikolainen, A.-L., Pérez-Caballero, F. & Koel, M. Low-density organic aerogels from oil shale by-product 5-methylresorcinol. *Oil Shale*, in press.
18. Mandel, F. S. & Don Wang, J. Manufacturing of specialty materials in supercritical fluid carbon dioxide. *Inorg. Chim. Acta*, 1999, **294**, 214–223.
19. Moreno-Castilla, C. & Moldano-Hódar, F. J. Carbon aerogels for catalysis applications: An overview. *Carbon*, 2005, **43**, 455–465.

Nanostruktuurse süsinikaerogeeli valmistamine

Fernando Pérez-Caballero, Anna-Liisa Peikolainen ja Mihkel Koel

Väikese tihedusega süsinikaerogeelide valmistamisel on suurepäraseks lähteaineks väikese tihedusega orgaanilised aerogeelid. Artiklis on kirjeldatud 5-metüülresortsinool-formaldehüüdgeelist aerogeeli saamise meetodikat, mis seisneb geeli kuivatamises ülekritilise süsinikdioksiidiga ja võimaldab vältida geeli poorsust tugevalt kahandavaid kapillaarjõude, ning süsinikaerogeeli saamise meetodikat, mille kohaselt orgaaniline aerogel pürolüüsitakse inertses lämmastiku keskkonnas. On uuritud geeli koostist ja struktuuri ning mõõtmete vähenemist süsinikaerogeeli saamise erinevatel etappidel; on mõõdetud tihedust, poride keskmist läbimõõtu ja eripinna suurust.